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(54) Fungicidal composition for agricultural use

(57) A fungicidal composition for agricultural use comprises 5-methyl-s-triazolo(3,4-b)benzothiazole, a clay mineral and an oleophilic base which is solid at ambient temperature. The preferred weight proportions of the components are 0.5—60:10—90:10—60. The composition is a granular preparation, which is long-acting for the protection of rice plants from blast, and has much reduced phytotoxicity to rice plants. The compositions may be made by melting the oleophilic substance, mixing with the other components and granulating.

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SPECIFICATION

Fungicidal c mp siti n for agricultural use

The present invention relates to a fungicidal composition for agricultural use. More particularly, it relates to an agricultural fungicidal composition formulated in a granular preparation which comprises 5-methyl-s-triazolo-(3,4-b)benzothiazole (hereinafter referred to as "Compound A"), a clay mineral and an oleophilic base which is a solid ambient temperature. The compound A is disclosed in Japanese Patent Publication (unexamined) No 61499/73.

Rice is the staple cereal crop of Asia, and the most serious disease of rice plants is blast. Various chemicals are available for control of rice blast but none of them has proved fully satisfactory. Thus, some of them do not provide adequate fungicidal effects, others are not sufficiently long-acting, and others are toxic to plants, man and animals, fish and shell-fish, and so on.

An ideal procedure for reducing the time and labor necessary for blast control would consist in the treatment of rice plants at the young seedling stage so as to reduce or remove the need for pest control after transplantation from nurseries. However, to meet that objective, it is necessary and desirable that there be available an agricultural fungicidal composition which is not only highly active against the causative fungus of rice blast but is less phytotoxic, and long-acting.

When Compound A is formulated into an agricultural preparation such as wettable powders, granules, etc. by a conventional procedure and such preparation is applied to a nursery box housing young rice plants before transplanting, the rice plants undergo, within a few days, yellowing of the leaf tops depending on the environmental conditions, and death in extreme cases. Although the surviving rice plants when transplanted into a paddy field display resistance to blast for about 40 days after transplantation, their resistance is quite inadequate in the period of from the end of said 40 days to the completion of "heading" and subsequent maturing. This period following the said 40 day period is a time having important implications for rice plants, during which not only their vegetative growth but also their tiller-formation, heading and maturing take place. If rice plants succumb to blast during that period, they suffer serious damage.

As the result of the extensive study to overcome the above problems, it has been found that when Compound A is formulated together with a clay mineral and an oleophilic base in a solid state at atmospheric temperature into a granular preparation and this granular preparation is either directly applied to young rice seedlings in a nursery box or used in admixture with the nursery soil, the plants continue to display excellent resistance to blast after transplanting and even after heading. Although wettable powders or granules comprising Compound A as prepared by a conventional procedure often cause phototoxicity problems resulting in delayed growth, the said granular preparation produces no material or only much reduced phytotoxicity in rice plants even if the concentration of Compound A therein is relatively high. Thus, when rice plants are treated once with the said granular preparation at the nursery stage, they can be protected from blast even if subsequent treatment is reduced or omitted.

The fungicidal composition of this invention comprises Compound A, a clay mineral and an oleophilic base and is formulated as a granular preparation.

The clay mineral may be any material which is understood as "clay mineral" or including "clay mineral" in the field of agricultural chemicals. Examples are clay, talc, zeeklite, diatomaceous earth, bentonite, kaolin, and vermiculite. These clay minerals are preferred to be finely divided so as to pass, for instance, a 300 mesh screen. The clay mineral preferably has a specific gravity of more than 1.

The oleophilic base which is a solid at a ambient temperature preferably has a relatively low melting point, for instance, from about 45 to 85°C. Examples of such oleophilic bases, are solid paraffins of petroleum origin which melt between about 45 and 85°C; waxes and waxy substances (e.g. Japanese wax, bees wax, carnauba wax); higher fatty acids, containing for instance about 12 to 22 carbon atoms (e.g. lauric acid, palmitic acid, myristic acid, stearic acid); higher alcohols, containing for instance about 14 to 20 carbon atoms (e.g. cetyl alcohol, stearyl alcohol), etc.

Other oleophilic bases which may be used are higher fatty acid glycerides, animal oils and fats such as beef tallow and lard, vegetable oils such as palm oil, hydrogenated oils such as hydrogenated fish oil, hydrogenated sperm oil, hydrogenated beef tallow oil and hydrogenated castor oil, etc. Refined paraffin waxes (m.p. 50 to 75°C) available from crude petroleum oil by steam distillation and vacuum distillation as well as microcrystalline wax are also employable. Powdery polyethylene which is obtainable by polymerization of ethylene and high polymers obtainable by addition polymerization of ethylene oxide and having a solidification point of not lower than 40°C (e.g. PEG 1500, PEG 4000, PEG 6000) may also be used. In addition, phenolic resins and vinyl chloride resins, which have low thermal deformation points, may be used in combination with said oleophilic base.

The proportion of Compound A, the clay mineral and the olephilic base may be usually 0.5—60: 10—90: 10—60 by weight, preferably 1—40: 20—70: 20—50 by weight.

The formulation of the fungicidal composition of the invention into a granular preparation may be effected by a conventional procedure.

One of the typical procedures comprises mixing th said three ssential components, if necessary, together with one or more optional components such as water and a binding agent and granulating the resulting mixture. For instance, the oleophilic base is melted by heating at a temperature above its

melting point, Compound A and the clay mineral are added and the resultant mixture is stirred well so as to obtain a uniform mixture. Alternatively, the oleophilic base is melted by heating and added portionwise to a mixture of Compound A and the clay mineral, followed by stirring to make the mixture uniform. The uniform mixture thus obtained is then processed into granules by melt granulation or spray granulation. Particularly when the oleophilic base is a higher fatty acid or a paraffin wax, the adoption of melt granulation by the use of a jet granulator is favourable.

Another typical procedure comprises granulating a mixture of Compound A and the clay mineral and coating the granules with the oleophilic base. For instance, particles of the clay mineral preferably having a size of 16 to 80 mesh are brought into contact with a solution of Compound A in a volatile solvent and then the volatile solvent is evaporated to give particles of the clay mineral adsorbing Compound A thereon. Alternatively, Compound A is admixed with particles of the clay mineral preferably having a size of 300 mesh or less, the resulting mixture is kneaded with water and a binder, and the resultant kneaded material is granulated, dried and sieved to give granules having usually a size of 10 to 250 mesh, preferably a size of 10 to 80 mesh. Onto the thus prepared granules, the oleophilic base molten by heating above the melting point is sprayed or applied portionwise, if necessary, while stirring so that the said granules are fully coated with the oleophilic base. In such coating processes, any conventional apparatus such as a coating pan may be used.

The fungicidal composition of this invention, preferably having a specific gravity of more than 1, may be applied to a nursery box when rice plants are at the young seedling stage, this mode of application being called "nursery application". Alternatively, the fungicidal composition may be blended with nursery soil before it is filled into such a nursery box, this mode of application being called "pre-emergence application", followed by sowing, nursing and transplanting. Aside from such nursery application or pre-emergence application, or in addition thereto, the fungicidal composition may be applied to the standing water over the paddy field as is conventionally practised.

The amount of the fungicidal composition to be applied varies greatly with the environmental conditions, the proportion of the components in the fungicidal composition, etc. and is usually from about 5 to 5000 g, preferably from about 10 to 200 g, as Compound A, to 10 areas.

The fungicidal composition of this invention brings about considerable reductions in control time and labor, a significant increase in the duration of efficacy and an avoidance of the possible reduction of efficacy by the weather. Furthermore, it is low in phytotoxicity and, because the active ingredient is applied only to necessary sites, the efficiency of blast control is enhanced. There is no problem in scattering the fungicidal composition, nor is any special application machine and diluent water required. Thus, the fungicidal composition of this invention can be employed in any paddy field. It should be noticed, too, that the fungicidal composition is safe to fish and animals. Still, in the fungicidal composition of this invention, there may be included, in addition to the said three essential components, fertilizers, e.g. urea, ammonium nitrate, etc. as well as other agriculturally effective agents and auxiliary farm chemicals.

Thrcughout the present specification, the term "mesh" is intended to mean a Tyler mesh.

The following examples are given to illustrate this invention in further detail. Part(s) and % are by weight, unless otherwise indicated.

EXAMPLE 1.

(1) Forty parts of Compound A pulverized by a pulverizer to a particle size of 300 mesh pass were gradually added to 420 parts of paraffin (m.p. 52—58°C; manufactured by Wako Pure Chemicals Co., Ltd.) previously melted at about 80°C. To ensure an even suspension, the mixture was mixed in a homogenizer. Then, 540 parts of finely divided clay were gradually added thereto and similarly dispersed. The mixture was heated to about 80°C, whereby a viscous slurry was obtained. This slurry was jet-granulated by means of a jet granulator (manufactured by Kawasaki Heavy Industries, Ltd.) and sieved to obtain bead-shaped granules in a size of 10 to 48 mesh. The content of Compound A in this granular preparation was 4%.

(2) The above procedure was repeated except that 100 parts of Compound A, 420 parts of paraffin and 480 parts of finely divided clay were used. By this procedure, there was obtained a granular preparation having a Compound A content of 10%.

EXAMPLE 2.

(1) Forty parts of Compound A, previously pulverized to 300 mesh or less, were gradually added to 300 parts of stearic acid (m.p. 53—59°C; manufactured by Nippon Yushi K.K.) melted at 100°C. The mixture was stirred with warming to obtain an even dispersion, to which 660 parts of finely divided clay were gradually added. This mixed suspension was jet-granulated as in Example 1 to obtain bead-shaped granules having a particle size of 0.5 to 2.0 mm. The content of Compound A in this granular preparation was 4%.

(2) The same procedure as above was repeated except that 100 parts of Compound A, 300 parts of stearic acid and 600 parts of finely divided clay were used. By this pr cedure, there was obtained a granular preparation having a Compound A content of 10%.

EXAMPLE 3.

(1) By means of a V-mixer, 40 parts of Compound A, 40 parts of cartap hydrochloride (1,3-bio(carbamoylthio)-2-(n,n-dimethylamino)propane hydrochl ride; an insecticide manufactured by Takeda Chemical Industries Limited and 620 parts of finely divided clay were blended, and the resultant mixture was gradually added to 300 parts of a hot melt of stearic acid (m.p. 53—59°C; manufactured by Nippon Yushi K.K.). The mixture was granulated as in Example 1 (1) to obtain a granular preparation having a Compound A content of 4%.

(2) The above procedure was repeated except that 100 parts of Compound A, 40 parts of 2-iso-propylphenyl-N-methylcarbamate, 560 parts of finely divided clay and 300 parts of stearic acid were used. By the above procedure, there was obtained a granular preparation having a Compound A content of 10%.

EXAMPLE 4.

(1) Compound A was dry-milled in a hammer-mill to obtain finely divided powders which passed through at 325 mesh sieve. By means of a V-mixer, 40 parts of this finely divided powders of Compound A were blended with 600 parts of finely divided clay, and the mixure was gradually added to a mixture of 210 parts of paraffin wax (m.p. 58°C; manufactured by Nippon Seiro K.K.) and 150 parts of stearic acid (m.p. 53—59°C; manufactured by Nippon Yushi K.K.) previously melted at 110°C. To obtain an even dispersion, the mixture was stirred with a hand-mixer and then granulated by means of a jet-granulator as used in Example 1 (1). The granules were sieved to obtain bead-shaped granules having a particle size of 0.5 to 1.7 mm. The content of Compound A in this granular preparation was 4%.

(2) The above procedure was repeated except that 100 parts of Compound A, 540 parts of finely divided clay, 210 parts of paraffin wax and 150 parts of stearic acid were used. By the above procedure, there was obtained a granular preparation having a Compound A content of 10%.

EXAMPLE 5.

(1) Four-hundred parts of beef tallow fatty acid (m.p. 42°C; manufactured by Nippon Yushi K.K.) were heat-melted and, while hot, 5 parts of polyoxyethylene nonylphenylether were added thereto. This was followed by gradual addition of 40 parts of finely divided powders of Compound A and 555 parts of precipitated calcium carbonate while stirring. The viscous slurry thus obtained was filled into an injection syringe while hot and dispensed dropwise through the needle attached to the syringe into water. After the dropwise injection had been completed, the resultant granules were collected and sieved through 10 mesh and 32 mesh standard sieves to obtain a bead-shaped granular preparation. The content of Compound A in this granular preparation was 4%.

(2) By means of a ribbon mixer, 100 parts of finely divided powders of Compound A were admixed with 100 parts of crystalline urea and 400 parts of finely divided clay. This mixture was gradually added to 400 parts of a hot melt of paraffin wax (m.p. 46°C; manufactured by Nippon Seiro K.K.). The mixture was stirred in a homogenizer, and the resultant suspension was jet-granulated as in Example 5 (1) to obtain bead-shaped granules having a particle size of 0.5 to 2.0 mm. The content of Compound A in this granular preparation was 10%.

EXAMPLE 6.

(1) Forty parts of finely divided powders of Compound A were blended well with 150 parts of bentonite and 510 parts of finely divided clay, and the mixture was gradually added to 300 parts of a hot melt of stearic acid (reagent grade; manufactured by Wako Pure Chemicals Co., Ltd.). The mixture was evenly dispersed with a hand-mixer and spread on a flat-bottomed vessel, where it was solidified into a plate 1 mm thick. This plate was put in a mortar cooled with cold water of 10°C and crushed with a stirring rod. The crushed product was sieved through standard sieves of 9 mesh (2.0 mm) and 42 mesh (0.35 mm) to remove excessively coarse and excessively fine fractions. By the above procedure, there was obtained a granular preparation having a Compound A content of 4%.

(2) The above procedure was repeated except that 100 parts of Compound A, 150 parts of bentonite, 300 parts of stearic acid and 450 parts of finely divided clay were used. The resultant granular preparation had a Compound A content of 10%.

REFERENCE EXAMPLE 1.

To 4 parts of finely divided powders of Compound A wer added 7 parts of dry powders of α-starch as a binder, followed by blending with 89 parts of finely divided clay. The mixture was kneaded with an appropriate amount of water and granulated by means of an extrusion-granulator (screen diameter, 1.0 mm). After drying, the granules w re sieved to obtain a granular preparation having a size of 10 to 40 mesh.

REFERENCE EXAMPLE 2.

To 75 parts of finely divided powders of Compound A were added 5 parts of sodium laurylsulfate as a wetting agent, followed by addition of 4 parts of sodium ligninsulfonate as a dispensing agent. To this mixture were added 16 parts of finely divided clay, and the whole mixture was blended thoroughly in a ribbon mixer to prepare a wettable powder preparation of Compound A.

Test Example 1.

I. Test procedure

1) Cultivation of seedlings:

Rice plants (variety: Koshihikari) in the 2.3-leaf stage, cultivated in nursery boxes (30 x 60 x 3 cm), were used for the test.

2) Treatment:

The granular preparations produced in the preceding examples were tested. Thus, each preparation was applied to the surface of nursery box soil on the day before transplantation.

3) Cultivation of rice plants and assay of blast control activity:

On the day just after the treatment, rice plants were transplanted in Wagner pots (1/500 are) and grown in a greenhouse. The pots were transferred to another greenhouse in which plants were heavily-infected with blast to induce spontaneous infections, and the blast control effects were evaluated.

II. Test results

It will be apparent from Table 1 that the fungicidal composition of this invention provides a lasting blast control effect, i.e. over a period of no less than 56 days after transplantation, even if applied only once to the nursery box.

TABLE 1 Blast control

Test composition	Compound A in composition (%)	Amount of Compound A per box (g)	Leaf blast control score (%) *1)	
			43 Days after transplantation	56 Days after transplantation
Untreated (control)	—	—	0	0
Example 1				
(1) granules	4.0	4.0	84	74
(2) granules	10.0	10.0	95	87
Example 2				
(1) granules	4.0	4.0	91	83
(2) granules	10.0	10.0	98	87
Example 3				
(1) granules	4.0	4.0	86	73
(2) granules	10.0	10.0	97	92
Example 4				
(1) granules	4.0	4.0	85	79
(2) granules	10.0	10.0	96	89
Example 5				
(1) granules	4.0	4.0	83	73
(2) granules	10.0	10.0	94	87
Example 6				
(1) granules	4.0	4.0	87	76
(2) granules	10.0	10.0	95	92
Isoprothiolan granules (control)	12.0	12.0	54	31
Probenazole granules (control)	8.0	8.0	33	29

Note: Control score (%) = $\frac{\text{Percentage of the leaf blast lesion for treated group}}{\text{Percentage of the leaf blast lesion for untreated group}} \times 100$

Test Example 2.

I. Test procedure

1) Cultivation of rice seedlings:

The procedure described in Test Example 1 was followed.

2) Treatments:

The procedure described in Test Example 1 was followed.

3) Cultivation and assay of blast control activity:

On the day just after treatment with the test composition, the seedlings were transplanted into rectangular pots of polyvinyl chloride (40 x 80 x 30 cm) and grown in a greenhouse. On the 54th day after transplantation, the pots were transferred to a "vinyl-house" and near a heavily infected bed (1 mm x 15 m) to induce spontaneous infections with blast. On the 64th day and the 90th day after transplantation, the plants were examined to evaluate the control activity of the test composition.

II. Test results

It will be apparent from Table 2 that the fungicidal composition of this invention as applied once to nursery boxes on the day immediately preceding the day of transplantation, displayed very strong control activity not only against leaf blast but also against ear blast.

TABLE 2 Blast control

Test composition	Compound A in composition (%)	Amount of Compound A per box (g)	Leaf blast Control score (%) 64 Days after transplantation	Ear blast Control score (%) 90 Days after transplantation
Untreated (control)	–	–	0	0
Example 1				
(1) granules	4.0	4.0	87	87
(2) granules	10.0	10.0	95	96
Example 2				
(1) granules	4.0	4.0	96	90
(2) granules	10.0	10.0	99	97
Example 3				
(1) granules	4.0	4.0	97	90
(2) granules	10.0	10.0	99	96
Example 4				
(1) granules	4.0	4.0	90	89
(2) granules	10.0	10.0	96	92
Example 5				
(1) granules	4.0	4.0	90	91
(2) granules	10.0	10.0	99	97
Example 6				
(1) granules	4.0	4.0	87	93
(2) granules	10.0	10.0	96	94

Test Example 3.

I. Test procedure

1) Cultivation of rice seedlings:

The procedure described in Test Example 1 was followed.

2) Treatment:

On the day just before sowing, commercial nursery soil was blended with test composition in a given ratio.

3) Cultivation of rice plants and assay of blast control activity:

On the day just after treatment, 200 g of rice seeds were sowed per nursery box and cultivated. On the 18th day after sowing, the seedlings were inoculated by spraying a spore suspension of *Pyricularia oryzae* from a potato-sucrose-agar culture, and the blast control activity of the test composition was assayed. On the 22nd day after sowing, seedlings (which were healthy) were transplanted into Wagner pots (1/500 are) and grown in a greenhouse. After transplantation, the pots were placed in a "vinyl-house" and near a heavily infected bed to induce spontaneous infections with blast. On the 28th day

and the 56th day after transplantation (corresponding to the 51th and the 57th day, respectively, after the treatment with the test composition), the rice plants were examined to evaluate the control action of the composition against leaf blast.

II. Test results

As will be seen from Table 3 wherein the symbol (—) means "negative in phytotoxicity", and the symbol (±) means "doubtful in phytotoxicity", the fungicidal composition of this invention, as applied to the soil prior to sowing, but only controls blast during growth in the nursery box but also controls leaf blast which would otherwise arise in the paddy field after transplantation.

TABLE 3 Blast control by nursery soil treatment

Test composition	Compound A in composition (%)	Amount of Compound A per box (g)	Percentage of leaf blast lesions (%)		
			19 Days after treatment (within nursery box)	28 Days after transplantation (51 days after treatment)	56 Days after transplantation (79 days after treatment)
Untreated (control)	–	–	80.0 (–)	10.0	11.5
Example 1					
(1) granules	4.0	4.0	14.5 (–)	3.0	2.7
(2) granules	10.0	10.0	6.5 (–)	1.7	0.9
Example 2					
(1) granules	4.0	4.0	3.5 (–)	1.7	4.2
(2) granules	10.0	10.0	2.0 (–)	1.0	1.5
Example 3					
(1) granules	4.0	4.0	2.0 (–)	2.0	3.3
(2) granules	10.0	10.0	2.0 (±)	0.7	1.5
Example 4					
(1) granules	4.0	4.0	6.5 (–)	3.0	4.2
(2) granules	10.0	10.0	5.0 (–)	1.7	1.0
Example 5					
(1) granules	4.0	4.0	8.0 (–)	2.3	4.2
(2) granules	10.0	10.0	2.0 (–)	1.3	1.5
Example 6					
(1) granules	4.0	4.0	6.5 (–)	2.3	3.3
(2) granules	10.0	10.0	5.0 (–)	0.7	2.1

Test Example 4

I. Test procedure

1) Variety:

Tainan #5; planted December 29, 1977, transplanted January 15, 1978.

2) Treatment:

The seedlings in a nursery box were treated with the test composition before transplantation. The granules were applied by scattering, while the wettable powders were suspended in water and applied by spraying. The seedlings in 20 such nursery boxes were transplanted next day in a 10-are field, and the degree of injury (phytotoxicity) and ear blast damage were respectively evaluated.

II. Test results

It will be apparent from Table 4 that, as applied once to nursery boxes before transplantation, the fungicidal composition of this invention even controls leaf blast and ear blast in paddy fields after tansplantation.

TABLE 4 Blast control in fields by a single treatment in a nursery box.

Test composition	Method of treatment	Amount of active agent per box (g)	Injury, 19 days after treatment *1)	Severity of ear blast, 113 days after treatment (control score, %) *2)
Untreated (control)	–	–	–	34.7 (0)
Example 1 (1) granules	Scattering granules	4.0	–	8.7 (75)
(2) granules	Scattering granules	10.0	–	6.4 (81)
Example 4 (2) granules	Scattering granules	10.0	–	3.5 (90)
Reference Ex. 1 granules	Scattering granules	4.0	+	13.5 (62)
Reference Ex. 2 wettable powders	Spraying suspension	5.33	++	17.4 (49)
EDDP emulsifiable concentrate (4 times treatments) *3)	Spraying emulsion	–	–	15.9 (54)

Notes: *1) Evaluation of phytotoxicity:–

–: Helathy leaf (no phytotoxicity)
+: Phytotoxic effect on about 20 to 30% of leaves
++: Phytotoxic effect on more than 30% of leaves

*2) Severity of ear blast (%) =

$$\frac{100}{3 \times (\text{the number of ears examined})} \times [3 \times (\text{the number of ears with rotton neck}) + 2 \times (\text{the number of ears with panicle blast lesion of about 2/3}) + 1 \times (\text{the number of ears with panicle blast lesion of about 1/3 to 2/3}) + 0.5 \times (\text{the number of ears with panicle blast lesion of about 1/3})]$$

*3) The EDDP emulsifiable concentrate (active component: 30%) was diluted 1000-fold with water and, after transplantation, was applied to plants 4 times, each at a rate of 150 L/10 are.

EXAMPLE 7.

(1) To 6 parts of Compound A, finely divided by means of a pulverizer, were added 5 parts of dry α-starch powder, and 89 parts of finely divided clay were added thereto, followed by thorough mixing. To the resulting mixture was added water, and the whole mixture was kneaded. The kneaded mixture was granulated by means of an extrusion-granulator with a screen diameter of 1.0 mm., followed by drying and size-selection. Five-hundred grams of the granules were put into a MARUMERAIZER® (Q—230 Type; manufactured by Fuji Paudal Co., Ltd.), in which 250 g of paraffin (m.p. 52—58°C; manufactured by Wako Pure Chemicals Co., Ltd.), melted by heating at about 70°C, were dripped from the overhead part of the apparatus with tumbling. The coated granules were further tumbled and, after cooling to room temperature, taken out of the apparatus. These granules were 16 to 32 mesh in size and contained Compound A in a concentration of 4%.

(2) In the same manner as (1), granules containing 10% of Compound A were prepared from 15 parts of Compound A, 80 parts of clay and 5 parts of α-starch.

(3) In the same manner as (1), granules containing 20% of Compound A were prepared from 30 parts of Compound A, 5 parts of α-starch and 65 parts of clay.

(4) In the same manner as (1), granules containing 40% of Compound A were prepared from 60 parts of Compound A, 5 parts of α-starch and 35 parts of clay.

EXAMPLE 8.

Twenty grams of the granules obtained in Example 7 (1) were put in a beaker, to which 20 g of paraffin (m.p. 52—58°C; manufactured by Wako Pure Chemicals Co., Ltd.) were added. The paraffin in the beaker was melted on a water-bath at about 80°C with stirring. After the paraffin had been melted, the water-bath was removed, and 10 g of the melted paraffin were discarded. The contents of the beaker were cooled to room temperature under mild stirring with a glass stick. The agglomerates were removed, whereupon granules coated with paraffin in a size of 10 to 40 mesh were obtained.

EXAMPLE 9.

(1) By the use of a spray-gun, 940 g of size-selected granular bentonite were uniformly sprayed with 300 g of a 20% chloroform solution of Compound A. After evaporation of the chloroform at room temperature, 20 g of the resultant granular bentonite containing Compound A were treated as in Example 8 to obtain granules coated with paraffin, which contained 4% of Compound A.

(2) In the same manner as (1) except that Compound A was used in a larger amount, paraffin-coated granules containing 10% of Compound A were prepared.

(3) In the same manner as (1) except that Compound A was used in a larger amount, paraffin-coated granules containing 20% of Compound A were prepared.

(4) In the same manner as (1) except that Compound A was used in a larger amount, paraffin-coated granules containing 40% of Compound A were prepared.

EXAMPLE 10.

Six-hundred grams of the granules obtained in Example 7(1) were further processed as in Example 7 except that 300 g of myristic acid (m.p. 58°C; manufactured by Wako Pure Chemicals Co., Ltd.) were used in place of paraffin. By the above procedure, there were obtained granules coated with myristic acid.

EXAMPLE 11.

Six-hundred grams of the granules obtained in Example 7(1) were further processed as in Example 7 except that 300 g of polyethylene glycol 6000 (m.p. 59°C; manufactured by Wako Pure Chemicals Co., Ltd.) were used in place of paraffin. By the above procedure, there were obtained granules coated with polyethylene glycol.

Reference Example 3.

To 4 parts of finely divided powders of Compound A were added 7 parts of dry α-starch powder together with 89 parts of finely divided clay, followed by mixing. To the resulting mixture was added an appropriate amount of water, and the whole mixture was kneaded. The kneaded mixture was granulated by an extrusion-granulator with a screen diameter of 1.0 mm, followed by drying and size-selection. By the above procedure, there were obtained granules in a size of 10 to 42 mesh.

Reference Example 4.

To 75 parts of finely divided powders of Compound A were added 5 parts of sodium lauryl sulfate as a wetting agent, 4 parts of sodium ligninsulfonate as a dispersing agent and 16 parts of finely divided clay, and the whole mixture was blended thoroughly in a ribbon mixer to prepare wettable powders of Compound A.

Test Example 5.

I. Test procedure

1) Cultivation of seedlings:

Rice seedlings (variety: Koshihikari) in the 2.2-leaf stage, cultivated in a nursery box (30 x 60 x 3 cm), were used for the test.

2) Treatment:

The granules of Example 7(1), the granules of Reference Example 3 and the wettable powders of Reference Example 4 were tested, the latter two preparations being used as controls. Each of the compositions was used in an amount of 3.75 g, as Compound A, per nursery box. The treatment with each composition was carried out on the day just before transplantation.

3) Cultivation of rice plants and assay of blast control activity:

Rice plants were transplanted into Wagner pots (porcelain pots) (1/500 are) on the day just after treatment, followed by cultivation in a greenhouse. After transplantation, a spore suspension of *Pyricularia oryzae* from a potato-sucrose-agar culture was used to inoculate the rice plants by spraying, and the blast control effect of each composition was investigated.

II. Test results

As shown in Table 5, the fungicidal composition of this invention continues to control the disease for more than 60 days, and it is clear that the composition is sufficiently effective throughout the period necessary for leaf blast control.

TABLE 5 Blast control

Days after transplantation	Percentage of leaf blast lesion (%) (days)					
	10	20	30	40	50	60
Untreated (control)	76.1	80.5	63.5	60.8	38.2	40.5
Granules of Ex. 7 (1)*1)	9.2	3.3	3.1	4.8	4.2	3.5
Granules of Ref. Ex. 3 *2)	1.4	6.2	8.3	10.2	17.2	20.2
Wettable powders of Ref. Ex. 4 *3)	0.5	5.4	15.9	10.6	20.6	25.1

Notes: *1) Content 4%; 3.75 g, as Compound A, per box

*2) Content 4%; 3.75 g, as Compound A, per box.

*3) Content 75%, 3.75 g, as Compound A, per box.

Test Example 6.

I. Test procedure

The procedure of Test Example 5 was repeated except that after transplantation into Wagner pots (porcelain pots) the rice plants were left in the open air. Transplantation were invariably carried out in the 13th day of July. Still, the heading occurred on the 1st day of September.

II. Test results

As shown in Table 6, the fungicidal composition of this invention was applied on the 12th day of July, i.e. the day just before transplantation. However, the activity of the composition to control leaf blast, which was investigated on the 5th day of September, and the activity thereof to control ear blast, which was investigated on the 30th day of September and the 18th day of October, were both excellent, surpassing the results achieved with the granules of Reference Example 3 and the wettable powders of Reference Example 4. Further, there was no symptom of phytotoxicity even when the composition of this invention was applied in an amount of 40 g, as Compound A, per box.

TABLE 6 Blast control effects in rice

Test composition	Compound A in composition (%)	Amount of Compound A per box (g)	Leaf blast				Ear blast	Leaf blast		Ear blast	Ear blast
			The date of inoculation with blast fungus after transplantation								
			14th day					28th day			49th day
			The date of investigation of lesions *1)								
			8/4	8/12	8/26	9/5	9/30	8/26	9/5	9/30	10/18
Untreated (control)	—	—	24.2	63.3	83.3	96.6	No heading	11.1	20.3	90.5	66.6
Example 7											
(1) granules	4.0	4.0	1.0	2.8	5.8	7.2	6.1	1.5	4.0	12.0	14.3
(2) granules	10.0	10.0	1.8	9.0	9.5	10.5	3.9	1.5	3.3	6.6	5.9
(3) granules	20.0	20.0	0.6	2.8	4.3	5.0	10.6	1.5	2.5	7.9	13.3
(4) granules	40.0	40.0	0.8	2.5	7.3	5.7	11.59	1.5	2.0	13.8	1.8
Granules of Ref. Ex. 3	4.0	4.0	0.4	6.5	8.8	12.7	38.1	3.5	6.0	43.6	64.7
Wettable powders of Ref. Ex. 4	75.0	3.75	0.8	8.0	14.5	19.7	47.2	8.0	7.5	61.6	66.6

Notes: *1) Dates are on a month/day basis.

Test Example 7.

I. Test procedure

The procedure of Test Example 6 was repeated except that the rice plants treated with the test composition were grown in a paddy field after transplantation.

II. Test results

It will be seen from Table 7 that by a single application of the fungicidal composition of this invention to the nursery box, both leaf blast and ear blast in the paddy field were almost completely inhibited.

TABLE 7 Blast control effects in rice *1)

Test composition	Compound A in composition (%)	Percentage of leaf blast lesion (%)	Percentage of ears with ear blast (%)				The severity of ear blast (%)
			30 Days after heading (83 days after transplantation)				
		On the 53rd day after transplantation	Neck blast	Panicle blast			46 Days after heading (99 days after transplantation)
				>2/3	2/3–1/3	1/3	
Untreated (control)	–	11	69.0	12.7	1.5	0	83.7
Granules of Ref. Ex. 3	4	6.1	21.8	16.7	6.0	0	44.6
Wettable powders of Ref. Ex. 4	70	5.9	37.4	6.6	6.4	0	50.5
Example 7							
(1) granules	4	0.7	3.6	5.0	5.1	0.5	14.6
(2) granules	10	0.3	0.5	1.0	1.3	0.4	3.3
(3) granules	20	0.2	0.5	0.5	0.6	0.7	2.4
(4) granules	40	0.2	0.5	0.9	0.4	0.6	2.4

Note: *1) Treatment of a nursery box of seedlings with the composition was carried out on the 11th day of July, and the transplantation thereof into a paddy field was carried out on the 12th day of July. The extent of infection with panicle branch blast was classified on the three-point scale of 2/3, 2/3 to 1/3 and 1/3.

Test Example 8

I. Test procedure

The procedure of Test Example 5 was repeated. However, the test composition was applied as blended with nursery box soil just before sowing. During the cultivation of seedlings and after the transplantation thereof into plastic pots, inoculation with blast fungus was carried out, and the blast control effect was investigated.

II. Test results

It is clear from Table 8 that by a single application of the fungicidal composition of this invention to the nursery box, both leaf blast and ear blast in the paddy field were effectively inhibited.

TABLE 8 Blast control effects in rice *1)

Test composition	Compound A in composition (%)	Amount of Compound A per box (g)	Percentage of leaf blast lesion (%)			Percentage of ears with ear blast (86 days after transplantation) (%)				
			Time after transplantation (days)							
			17	29	39					
			Time after blending (days)							
			31	42	52	Neck blast	Panicle blast			
							>2/3	2/3–1/3	1/3>	Total
Untreated (control)	–	–	3.4	8.8	34.8	81.3	4.5	0.5	0.2	86.5
Example 9										
(1) granules	4.0	4.0	0.6	1.0	4.0	6.0	4.4	1.3	2.1	13.8
(2) granules	10.0	10.0	0.4	0.4	1.9	3.6	1.6	0.4	0.8	6.4
(3) granules	20.0	20.0	0.2	0.1	1.0	2.9	0.9	0.4	0.9	5.1
(4) granules	40.0	40.0	0.4	0.1	2.0	1.4	0.9	0	0.4	2.7
Granules of Ref. Ex. 3	4.0	4.0	0.6	0.6	4.0	15.0	4.4	1.1	1.3	21.8
Wettable powders of Ref. Ex. 4	75.0	3.75	0.8	0.7	3.3	17.5	2.7	2.7	0.9	24.0

Note: *1) The blending of the composition with nursery bed soil was carried out on the 13th day of July, and the seeds were sowed just after the soil treatment. The transplantation was carried out on the 27th day of July (0.65 × 0.49 × 0.32 polyvinyl chloride containers). The heading occurred on the 16th day of September.

Test Example 9.

I. Test procedure

1) The area and the scale of the test:

Ichijoji, Sakyo-ku, Kyoto; a section of a paddy field as delimited by concrete framing; th area of which was about 1 m^2 and wherein 16 hills were planted. Each hill comprised 5 plants.

2) Variety, cultivation and infection of the plant:

Variety: Asahi No. 4.

The date of transplantation: the early stage of blast disease was observed in the period of from the 1st day of July to the 10th day of July.

The date of heading: the 25th day of August. Both leaf blast and ear blast were very serious.

3) Treatment with each test composition:

Submerged treatments with granules or wettable powders were carried out on the 6th day of July (the early stage of blast disease) and the 4th day of August (the 21th day before handling). The amounts of the compositions used are given in Table 9.

4) Investigation:

The severity of leaf blast was assessed in terms of the percentage of the affected area and rated according to the rating method of the Research Association of Systemic Fungicide Japan.

II. Test results

As is shown in Table 9, the submerged applications of the granules of Examples 10 and 11 provided superior blast control effects to those of the granules of Reference Example 3 and the wettable powders of Reference Example 4.

TABLE 9 Effect of controlling rice plant

Test composition	Compound A in composition (%)	Amount of application (10 kg of composition/10 ares)		Percentage of leaf blast lesion (%)		Percentage of ears with ear blast (%)
		Application for leaf	Application for ear	Investigated on July 14	Investigated on August 4	Investigated on September 27
Untreated (control)	—	—	—	1.3	20.9	87.6
Granules of Example 10	4.0	3	4	1.0	0.7	4.4
Granules of Example 11	4.0	3	4	1.2	1.1	2.0
Granules of Ref. Ex. 3	4.0	3	4	1.4	4.8	21.9
Wettable powders of Ref. Ex. 4	75.0	0.16	0.212	1.6	20.6	28.5

CLAIMS

1. A granular fungicidal composition which comprises 5-methyl-s-triazolo(3,4-b)benzothiazole, a clay mineral and an oleophilic base which is a solid at ambient temperature.

2. A fungicidal composition as claimed in claim 1, wherein the proportion of the 5-methyl-s-triazolo(3,4-b)benzothiazole, the clay mineral and the oleophilic base is 0.5—60: 10—90: 10—60 by weight.

3. A fungicidal composition as claimed in claim 2, wherein the proportion of the 5-methyl-s-triazolo(3,4-b)benzothiazole, the clay mineral and the oleophilic base is 1—40: 20—50 by weight.

4. A fungifical composition as claimed in any one of the preceding claims which has a specific gravity of more than 1.

5. A method of preparing a fungicidal composition which method comprises granulating a mixture comprising 5-methyl-s-triazolo(3,4-b)benzothiazole, a clay mineral and an oleophilic base.

6. A method of preparing a fungicidal composition which method comprises granulating a mixture comprising 5-methyl-s-triazolo(3,4-b)benzothiazole, and a clay mineral and coating the resulting granules with an oleophilic base which is a solid at ambinet temperature.

7. A method of preparing a fungicidal composition substantially as hereinbefore described in any one of the specific Examples.

8. A fungicidal composition when prepared by a process as claimed in any one of claims 5 to 7.

9. A fungicidal composition susbstantially as hereinbefore described in any one of the Examples.

10. A method for the control or prevention of rice blast in rice plants which comprises applying a composition as claimed in any one of claims 1 to 5, 8 or 9 to the plants or to a locus wherein the rice plants are cultivated or are to be cultivated.

11. A method as claimed in claim 10, wherein the composition is applied to soil wherein the seeds of rice plants are sown or are to be sown.

12. A method as claimed in claim 10, wherein the composition is applied to soil wherein rice plant seedlings are planted or are to be planted.

13. A method as claimed in claim 11 or claim 12, wherein the soil is in a nursery box.

14. A method as claimed in any one of claims 10 to 13, wherein the fungicidal composition is applied in an amount of about 5 to 5000 grams as the 5-methyl-s-triazolo(3,4-b)benzothiazole to 10 ares.

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